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54 **High strength heat bondable fibre.**

57 High strength spun melt fiber, preparation thereof utilizing selective threadline oxidative chain scission degradation of hot fiber spun from polymer component(s) with a delayed quench step, plus corresponding process and materials.

**EP 0 445 536 A2**

## HIGH THERMAL STRENGTH BONDING FIBER

Efficient, high speed spinning and processing of polyolefin fiber such as polypropylene requires careful control over the degree of chemical degradation and melt flow rate (MFR) of the spun melt, and a highly efficient quenching step for avoiding both over- or under-quench (i.e. melt fracture or ductile failure) during high speed commercial production.

5 This invention improves control over polymer degradation, spin and quench steps and obtains fiber or filament for producing nonwoven fabrics with increased strength, toughness, integrity and heat-bonding properties.

Such are obtained by use of a process characterized by the steps of

10 A. admixing an effective amount of at least one antioxidant/stabilizer into a spun melt comprising polyolefin polymer or copolymer and preferably a polymer having a broad molecular weight (wt. average/number average) distribution such as isotactic polypropylene, in the presence of a degrading agent. A suitable MFR (melt flow rate) for spinning being about 5-35, in the substantial absence of oxygen, oxygen-containing, or oxygen-evolving gases.

15 Various other additives known to the polymeric fiber spinning art can also be incorporated and applied, as desired, such as pigments, colorants, pH-stabilizers, lubricants and antistatic agents in usual amounts (i.e. about 1%-10% by weight or less);

B. spinning the spun melt at a temperature, preferably within a range of about 250° C.-325° C. for polypropylene, and atmospheric environment favoring little or no oxidative chain scission degradation of the polymeric component(s) within said spun melt during the spinning step;

20 C. taking up the resulting hot extrudate (poorly quenched or essentially unquenched filament) under an oxygen-rich atmosphere to obtain sufficient oxygen gas diffusion to effect a threadline oxidative chain scission degradation of the hot extrudate or filament; and

25 D. fully quenching and finishing the resulting filament to obtain a highly degraded surface zone of low molecular weight and low birefringence; and a minimally degraded, crystalline birefringent inner configuration, said two zones representing extreme configurations bounding and defining an intermediate zone (component (b) Figure 1) of intermediate polymeric oxidative degradation and crystallinity, the thickness of which depends essentially upon fiber cross-sectional structure and the rate of cooling of the hot extrudate or filament and oxygen concentration.

30 A fiber or filament of this invention preferably utilizes "broad molecular weight" polyolefin polymer or copolymer such as a polypropylene-containing spun melt having incorporated therein an effective amount of at least one antioxidant/stabilizer composition, the resulting fiber or filament, when quenched, comprising, in combination (ref. Figure 1),

(a) an inner zone, shown schematically as a cross-section in Figure 1, is identified by minimal oxidative polymeric degradation, high birefringence, and a weight average molecular weight conveniently within a range of about 100,000-450,000 and preferably within about 100,000-250,000;

(b) an intermediate zone generally externally concentric to the described inner zone and further identified by progressive (inside-to-outside) progressive oxidative chain scission degradation, the polymeric material within the intermediate zone having a molecular weight gradation less than the "a" zone of Figure 1 down to a minimum range of less than about 20,000 and preferably about 10,000-20,000; and

40 (c) a surface zone generally externally concentric to the intermediate zone and defining the external surface of the spun fiber or filament, such surface zone being identified by low birefringence, a high concentration of oxidative chain scission-degraded polymeric material, and a weight average molecular weight of less than about 10,000 and preferably about 5,000-10,000.

Figure 2 schematically represents cross-section of a corresponding bicomponent-type fiber or filament 45 zones in which (a'), (b') and (c') are defined substantially as counterparts of elements a-c of Figure 1, while element (d') represents a bicomponent core element of the same or different melt composition which is conveniently applied by use of a spin pack in a conventional manner, inner layer (a') being of a compatible (i.e. core-wettable) polymeric material. Core element, (d') is preferably formed and initially sheath-coated while in a substantially nonoxidative environment in order to avoid or minimize formation of a low-birefringent, low molecular weight interface between zones (d') and (a').

50 The sheath and core elements of bicomponent fiber can be conventionally spun in accordance with equipment and techniques known to the bicomponent fiber art (ref. U.S. Patent 3,807,917, 4,251,200, 4,717,325 and "Bicomponent Fibers", R. Jeffries, Merrow Monograph Publ. Co., '71), except for the preferred use of nitrogen or other inert gas environment to displace and minimize oxygen diffusion into the hot spun melt or the hot core element prior to application of a sheath component around it.

For present purposes the term "effective amount", as applied to the concentration of antioxidant/stabilizer compositions within the dry spun melt mixture, is defined as an amount, based on dry weight, which is capable of preventing or at least substantially limiting chain scission degradation of the hot polymeric component(s) within fiber or filament-spinning temperature range, assuming the substantial absence of oxygen, an oxygen evolving, or an oxygen-containing atmosphere. In particular, a concentration of one or more antioxidant compositions sufficient to effectively limit chain scission degradation of polyolefin component of a heated spun melt composition within a temperature range of about 250° C. to about 325° C., in the substantial absence of an oxidizing environment such as oxygen, air or other oxygen/gas mixtures. The above definition, however, permits a substantial amount of oxygen diffusion and oxidative polymeric degradation commencing at or about the melt zone of the spun fiber threadline and extending downstream to a point where natural heat loss and/or an applied quenching environment lowers the fiber surface temperature to a point where oxygen diffusion into the spun fiber or filament is negligible (250° C or below for polypropylene polymer or copolymer).

Generally speaking, the total combined antioxidant/stabilizer concentration usually falls within a range of about .002%-1% by weight, and preferably within a range of about .005%-0.5%, the exact amount depending on the particular rheological and molecular properties of the chosen broad molecular weight polymeric component(s) and the temperature of the spun melt; additional parameters are represented by temperature and pressure within the spinnerette itself, and the amount of prior exposure to residual amounts of oxidant such as air while in a heated state upstream of the spinnerette. Below or downstream of the spinnerette an oxygen/nitrogen gas flow ratio of about 100:10:0-90 by volume at an ambient temperature up to about 200° C. plus a delayed quench step are preferred to assure adequate chain scission degradation of the polymer component and to provide improved thermal bonding characteristics, leading to increased strength, elongation and toughness of nonwovens formed from the corresponding continuous fiber or staple.

The amount of degrading composition used can extend from 0% up to a concentration, by weight, sufficient to supplement the application of heat and pressure to the spun melt mix and obtain a spinnable MFR (melt flow rate) value. Assuming the preferred use of a broad molecular weight distribution of polypropylene-containing spun melt, this constitutes an amount which, at a melt temperature range of 275° C.-320° C. and in the substantial absence of oxygen or oxygen-containing or oxygen-evolving gas, is capable of obtaining a spun melt within a 5-35 MFR range.

Suitable antioxidant/stabilizer compositions, comprise one or more art-recognized antioxidant compositions inclusive of phenylphosphites such as Irgafos® 168, Ultrinox® 626<sup>(Ciba Geigy)</sup> Sandostab® PEP-Q<sup>(Sandoz Chemical Co.)</sup>; N,N'-bis-piperidiny diamine-containing compositions such as Chimassorb® 119 or 944<sup>(American Cyanamid Co.)</sup>; hindered phenolics such as Cyanox® 1790<sup>(American Cyanamid)</sup>, Irganox® 1076 or 1425<sup>(Ciba Geigy)</sup> and the like.

The term "quenching and finishing", as here used, is defined as a process step generic to one or more of the steps of gas quench, fiber draw (primary and secondary if desired) and texturing, (optionally inclusive of one or more of the routine steps of bulking, crimping, cutting and carding), as desired.

Typical spun fiber or filament obtained in accordance with the present invention can be continuous and/or staple fiber, such fiber being shown schematically in cross-section in the accompanying Figures as a monocomponent- (Figure 1) or bicomponent- (Figure 2) type, the inner zone in the former, having a relatively high crystallinity and birefringence with negligible or very small polymeric oxidative chain scission degradation.

In the bicomponent-type fiber or filament, the corresponding inner layer of the sheath element is comparable in physical condition to the center cross sectional area of a monocomponent fiber, however, the bicomponent core element is not necessarily treated in accordance with the instant process or even consist of the same polymeric material as the sheath component, although preferably compatible with and wettable by the polymer forming inner zone of the sheath component.

The above-described zones within Figures 1 and 2 are representative of the effect of the instant process on monocomponent and bicomponent fibers but the described zones are usually not visually ascertainable in test samples, nor can an even depth of oxygen diffusion throughout the treated fiber be assumed.

As above noted, the instant invention does not necessarily require the addition of a conventional polymer degrading agent in the spun melt mix, although such use is not precluded by this invention in cases where a low spinning temperature and/or pressure is preferred, or if, for other reasons, the MFR value of the heated polymer melt is otherwise too high for efficient spinning. In general, however, a suitable MFR (melt flow rate) for initial spinning purposes is best obtained by careful choice of a broad molecular weight polyolefin-containing polymer to provide the needed rheological and morphological properties when operating within a spun melt temperature range of about 275° C.-320° C. for polypropylene.

For present purposes a quenching of the bicomponent fiber is preferably delayed at the threadline, by

partially blocking the quench gas, and then providing air, ozone, oxygen, or other conventional oxidizing environment (heated or ambient temperature) further downstream to assure sufficient oxygen diffusion into the sheath element and oxidative chain scission within at least surface zone (c') and preferably both (c') and (b') zones of the sheath element (ref. Figure 2).

5 Yarns as well as webs for nonwoven material are conveniently formed from fibers or filaments obtained in accordance with the present invention by jet bulking, cutting to staple, crimping and laying down the fiber or filament in conventional ways and as demonstrated, for instance, in U.S. Patents 2,985,995, 3,364,537, 3,693,341, 4,500,384, 4,511,615, 4,259,399, 4,480,000, and 4,592,943.

10 While Figures 1 and 2 show generally circular fiber cross sections, the present invention is not so limited. Conventional diamond-, delta-, oval-, "Y-", "X-" and dog bone-shaped cross sections are equally treatable within the instant invention.

The present invention is further demonstrated, but not limited to the following Examples:

#### EXAMPLE 1

15 Dry melt spun compositions identified hereafter as SC-1 through SC-12 are individually prepared by tumble mixing linear isotactic polypropylene flake identified as "A"- "D" in Table I (Himont Incorporated) and having Mw/Mn values of about 5.4 to 7.8 and a Mw range of 195,000-359,000, which are admixed respectively with about 0.1% by weight of conventional stabilizer(s) (see above). The mix is then heated and  
20 spun as circular cross section fiber at a temperature of about 300° C. under a nitrogen atmosphere, using a standard 782 hole spinnerette at a speed of 750-1200 M/m. The fiber thread lines in the quench box are exposed to a normal ambient air quench (cross blow) with up to about 5.4% of the upstream jets in the quench box blocked off to delay the quenching step. The resulting continuous filaments, having spin denier within a range of 2.0-2.6 dpf, are then drawn (1.0 to 2.5X), crimped (stuffer box steam), cut to 1.5 inches,  
25 and carded to obtain conventional fiber webs. Three ply webs of each staple are identically oriented and stacked (machine direction), and bonded, using a diamond design calender at respective temperatures of about 157° C. or 165° C., and 240 PLI (pounds/linear inch) to obtain test nonwovens weighing 17.4-22.8 gm/yd<sup>2</sup>. Test strips of each nonwoven (1" x 7") are then identically conventionally tested for CD strength (tensile tester from Instron Incorporated) elongation and toughness based on stress/strain curve values. The  
30 fiber parameters and fabric strength are reported in Tables II-IV, below, using the polymers described in Table I, the "A" polymers being used as controls.

#### EXAMPLE 2 (Controls)

35 Example I is repeated, utilizing polymer A and/or other polymers with a low Mw/Mn of 5.35 and/or full (non-delayed) quench. The corresponding webs and test nonwovens are otherwise identically prepared and identically tested as in Example 1. Test results of the controls, identified as C-1 through C-9 are reported in Tables II-IV.

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TABLE I

Spun Mix Polymer Identification	$\bar{M}_w$ (g/mol)	Sec(*1) $\bar{M}_n$ (g/mol)	$\bar{M}_w/\bar{M}_n$	Intrinsic Visc. IV (deciliters/g)	MFR (gm/10 min)
5 A	229,000	42,900	5.35	1.85	13
B	359,000	46,500	7.75	2.6	5.5
C	290,000	44,000	6.59	2.3	8
D	300,000	42,000	7.14	2.3	8

(\*1) Size exclusion chromatography.

TABLE II

Melt Sample	Polymer	MWD	Spin Temp °C.	Area		Comments
				% Quench	Box*	
5	C-1	5.35	298	3.74	Blocked Off	Control
	SC-1	6.59	305	3.74		5.5 MWD
	SC-2	7.14	309	3.74		5.5 MWD
	SC-3	7.75	299	3.74		5.5 MWD
10	C-2	5.35	298	3.74		Control < 5.5 MWD
	C-3	5.35	300	3.74		Control < 5.5 MWD
	C-4	5.35	298	3.74		Control < 5.5 MWD
15	SC-4	7.14	309	3.74		No stabilizer
	SC-5	7.14	312	3.74		---
	SC-6	7.14	314	3.74		---
	SC-7	7.14	309	3.74		---
20	SC-8	6.59	305	5.38		Control/Full Quench
	SC-9	6.59	305	3.74		
	C-5	6.59	305	0		
	C-6	5.35	290	5.38		
25	C-7	5.35	290	3.74		Control < 5.5 MWD
	C-8	5.35	290	0		Control < 5.5 MWD
	SC-10	7.14	312	3.74		Control/Full Quench
	C-9	7.14	312	0		
25	SC-11	7.75	278	4.03		
	SC-12	7.75	299	3.74		
	SC-13	7.75	300	3.74		

TABLE III

FIBER PROPERTIES						
Melt Sample	MFR (dg/min)	MWD	dpf	Tenacity (g/den)	Elongation %	Comments
5	C-1	4.2	2.50	1.90	343	Effect of MWD
	SC-1	5.3	2.33	1.65	326	
	SC-2	5.2	2.19	1.63	341	
	SC-3	5.3	2.14	2.22	398	
10	C-2	4.6	2.28	1.77	310	Additives
	C-3	4.6	2.25	1.74	317	Effect
	C-4	4.5	2.48	1.92	380	Low MWD
	SC-4	5.4	2.28	1.59	407	High MWD
15	SC-5	5.1	2.33	1.64	377	Additives
	SC-6	5.6	2.10	1.89	357	Effect
	SC-7	5.6	2.48	1.54	415	
	SC-8	5.3	2.64	1.50	327	Quench
20	SC-9	5.3	2.33	1.65	326	Delay
	C-5	5.3	2.26	1.93	345	
	C-6	4.5	2.28	1.81	360	Quench
	C-7	4.5	2.26	1.87	367	Delay
25	C-8	4.5	2.28	1.75	345	
	SC-10	5.1	2.33	1.64	377	Quench
	C-9	5.2	2.18	1.82	430	Delay
	SC-11	5.4	2.40	2.00	356	---
25	SC-12	5.3	2.14	2.22	398	---
	SC-13	5.1	2.59	1.65	418	---

TABLE IV

FABRIC CHARACTERISTICS  
(Variation in Calender Temperatures)

			CALENDER	FABRIC			
	5	Melt	Temp	Weight	CDS	CDE	TEA
		Sample	(°C.)	(g/sq yd.)	(g/in.)	(%)	(g/in.)
10		C-1	157	22.8	153	51	42
		SC-1	157	21.7	787	158	704
		SC-2	157	19.2	513	156	439
15	10	SC-3	157	18.7	593	107	334
		C-2	157	18.9	231	86	106
		C-3	157	21.3	210	73	83
		C-4	157	20.5	275	74	110
20		SC-4	157	18.3	226	83	102
	15	SC-5	157	20.2	568	137	421
		SC-6	157	19.1	429	107	245
		SC-7	157	21	642	136	485
25		SC-8	157	19.8	498	143	392
		SC-9	157	21.7	787	158	704
	20	C-5	157	19.4	467	136	350
		C-6	157	19.1	399	106	233
30		C-7	157	19.8	299	92	144
		C-8	157	17.4	231	83	105
		SC-10	157	20.2	568	137	421
35	25	C-9	157	20.4	448	125	300
		SC-11	157	19.4	274	86	122
		SC-12	157	18.7	593	107	334
		SC-13	157	19.4	688	132	502



TABLE IV (Continued)

FABRIC CHARACTERISTICS  
(Variation in Calender Temperatures)

	5	Melt Sample	CALENDER Temp (°C.)	FABRIC Weight (g/sq yd.)	CDS (g/in.)	CDE (%)	TEA (g/in.)
10		C-1	165	20.3	476	98	250
		SC-1	165	22.8	853	147	710
		SC-2	165	19	500	133	355
15	10	SC-3	165	19.7	829	118	528
		C-2	165	18.8	412	120	262
		C-3	165	20.2	400	112	235
		C-4	165	20.6	453	102	250
20		SC-4	165	19.3	400	110	239
	15	SC-5	165	17.9	614	151	532
		SC-6	165	19.9	718	142	552
		SC-7	165	20.5	753	157	613
25		SC-8	165	20.4	568	149	468
		SC-9	165	22.8	853	147	710
	20	C-5	165	17.4	449	126	303
		C-6	165	18.5	485	117	307
30		C-7	165	19.7	482	130	332
		C-8	165	19.2	389	103	214
		SC-10	165	17.9	614	151	532
35	25	C-9	165	19.4	552	154	485
		SC-11	165	20.1	544	127	366
		SC-12	165	19.7	829	118	528
		SC-13	165	19.2	746	138	576

#### Claims

1. A fiber or filament generated from at least one spun melt mixture comprising a broad molecular weight polyolefin polymer or copolymer and containing an effective amount of at least one antioxidant/stabilizer composition, said fiber comprising, in combination,
  - (a) an inner zone identified by minimal oxidative polymeric degradation, high birefringence, and a weight average molecular weight within a range of about 100,000-450,000;
  - (b) an intermediate zone generally externally concentric to said inner zone and further identified by progressive oxidative chain scission degradation with a molecular weight gradation within a range of slightly less than said inner zone - to- about 10,000-20,000; and
  - (c) a surface zone generally externally concentric to said intermediate zone and defining the external surface of the spun fiber or filament, said surface zone being identified by low birefringence, a high concentration of oxidative chain scission-degraded polymeric material, and a weight average molecular weight of less than about 10,000.
2. A sheath/core bicomponent fiber of claim 1 wherein said inner zone is internally contiguous with and generally externally concentric to a core element.

3. A fiber or filament of claim 1 wherein said inner zone is an integral part of a monocomponent fiber, formed essentially from a common spun melt mixture.
4. A fiber of claim 1 wherein polymer component of said inner zone of the sheath element has a  
5 molecular weight of about 100,000-250,000, degraded polymer component of said intermediate zone has a molecular weight of about 100,000-250,000-down-to-less than 20,000 and degraded polymer component of said surface zone has a weight average molecular weight of about 5,000-10,000.
5. In a process for preparing monocomponent or bicomponent fiber from polyolefin-containing spun melt  
10 composition, the improvement comprising
  - A. admixing an effective amount of at least one antioxidant/stabilizer into a spun melt comprising polyolefin polymer or copolymer, in the presence of a degrading agent;
  - B. spinning the resulting spun melt at a temperature and atmospheric environment favoring minimal oxidative chain scission degradation of the polymeric component(s) within the spun melt during the  
15 spinning step;
  - C. taking up the resulting hot extrudate under an oxygen-rich atmosphere to obtain sufficient oxygen gas diffusion to effect a threadline oxidative chain scission degradation of the hot filament; and
  - D. fully quenching and finishing the resulting filament to obtain a highly degraded surface zone of low molecular weight and low birefringence; and a minimally degraded, high molecular weight,  
20 crystalline birefringent inner zone.
6. A process of claim 5 wherein the antioxidant/stabilizer composition is a phenyl phosphite- and/or a N,N'-bis-piperidinyI diamine derivative.
- 25 7. A process of claim 5 wherein the highly degraded surface zone of the spun fiber or filament has a weight average molecular weight of less than about 10,000, and the inner zone configuration of said spun fiber has a high birefringence and a weight average molecular weight within about 100,000-450,000.
- 30 8. A process of claim 5 wherein the take up step is carried out in the presence of oxygen at ambient temperature.
9. A process of claim 5 wherein the quenching step is carried out in the presence of an oxygen/nitrogen mixture varying in ratio by volume from about 100-10:0-90.
- 35 10. A nonwoven material obtained by bonding one or more web containing fiber or filament produced in accordance with the method of claim 5.
11. A nonwoven material obtained by bonding one or more web containing fiber produced in accordance  
40 with the method of claim 7.

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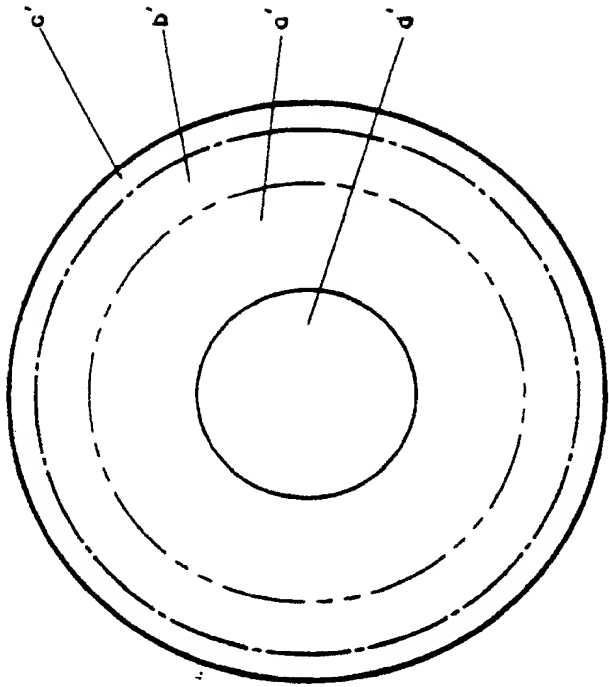


FIG. 2

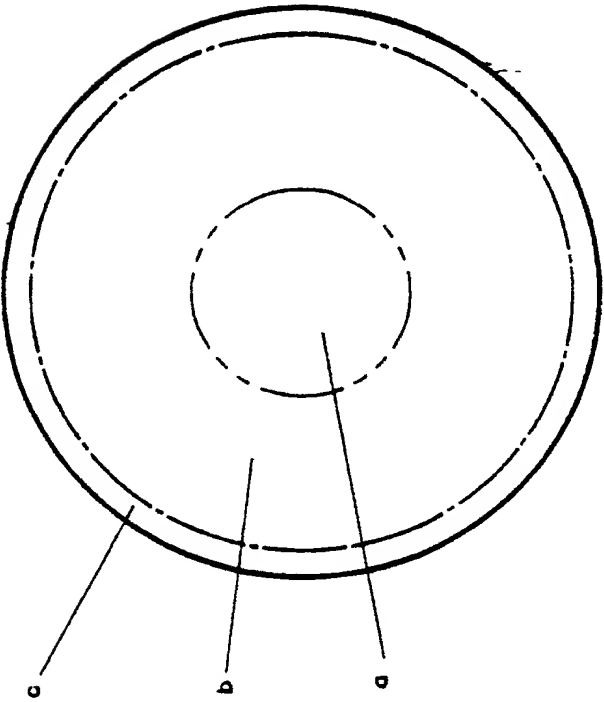


FIG. 1

**PUB-NO:** EP000445536A2  
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**ABSTRACT:**

CHG DATE=19990617 STATUS=O> High strength melt  
spun fiber; preparation thereof utilizing

selective, threadline oxidative, chain scission degradation of hot fiber spun from polymer component(s) with a delayed quench step, plus corresponding process and materials.